

-----Electroplating-----Dr. Savita Desai.

Electroplating or electrodeposition or electrode deposition is a branch of electrometallurgy. It is the art of depositing metals by means of an electric current on metallic or sometimes nonmetallic surfaces.

The electrode deposition finds its applications for the following purposes.

1. To add pleasing appearance to the nonattractive metals.
2. To provide protection against corrosion.
3. To put expensive components into continued service.
4. In military problems.

Basic Principles of electroplating:

Theories: When the potential difference is applied by means of suitable electrodes dipped in a solution of metallic salt, there is ionization of the salt.

(Electrolysis) The metallic ions migrate towards and deposit at the cathode. If the cathode is made up of a suitable metal, then the metal ions are formed and enter into the solution. This continues the deposition. In certain cases the use of insoluble anode is preferable and essential.

Practically, the ions have their own characteristic speed, due to which the process of deposition is slow, which is enhanced by mechanical agitation.(Movement/ circulation) of the electrodes.

Quantitative Electrodeposition/Fundamental Laws of electrolysis:

Faraday (1835)put forward the laws of electrolysis.

1. The wt of the metal deposited at an electrode is proportional to the quantity of electricity passed through the electrolyte.
2. When the same quantity of electricity is passed through different electrolytes, the wt of metal deposited is proportional to their chemical equivalents.

When one Faraday (96500 coulombs) of current is passed, there is deposition of 1 equivalent of the metal i.e.108 grams of Ag, etc.

However, under practical conditions, the deposition is less than the theoretical value (As given by Faraday's Law) hence, the terms cathode efficiency and anode efficiency are introduced.

Cathode efficiency = $\frac{\text{wt of metal actually deposited}}{\text{Wt of metal expected to be deposited}} \times 100$

= % Efficiency

Anode efficiency = $\frac{\text{wt of metal actually dissolved}}{\text{Wt of metal expected to be dissolved}} \times 100$

= % Efficiency

Electrical conditions: The surface to be coated is immersed in the solution of the salt of the metal to be deposited, which will act as a cathode. The anode of the metal to be

deposited is also immersed in the same solution. The current of 6 to 12 volts is provided. This high current density is sufficient to overcome the resistance of the solution.

Current density: it is the measurement of the current on the specific area. It is expressed in terms of amperes per square foot. In general, the uniform deposition is achieved by low current density. Increased current density upto certain limit improves fineness of the deposition. But more current density than the limit will cause rough porous or spongy deposits (called burnt)

Throwing power: Uneven surface has problems in electroplating. The area near the cathode may get heavily deposited. Hence, the anodes must be placed properly and the solution must have good throwing power, so that the metal is deposited in the recesses. This is obtained by using a cyanide or similar solution so that the excess metal is largely locked by complex ions. (The metal is thrown in the solution again in the form of a complex ion. Hence, it is throwing power)

Covering power: The capacity of the solution to cover the cathode surface is called covering power. It is related also to the throwing power and the lowest current density at which the metal can be deposited.

Concentration: The uneven porous /Spongy/ burnt deposits are overcome by increasing the concentration of the salt which plays an important role.

Agitation: The ions migrate towards the respective electrodes with their own speed, which will make the process of electroplating time consuming. Hence, the electrodes especially cathode is agitated. This also helps in sweeping away the gas bubbles formed during electrolysis.

But agitation beyond certain limits causes- 1. Rough deposits due to sedimentation of the metal in suspension. The metal ion cannot get sufficient time to get adsorbed on the cathode. Hence, metal particles remain suspended in the solution. 2. Decrease in throwing power. 3. Formation of carbonates (probably due to CO₂ entered in solution.) in cyanide solutions.

Temperature: Increasing temperature of the bath increases the roughness of the deposits. But in practice, warmed baths are used because of some advantages because it causes: 1. An increase in the solubility of the salts. It helps in using the high concentration and high current density. 2. An increase in the conductance, which reduces the tendency of treeing, lowers the cost of electricity.

Conductance: Good conductance reduces the voltage required for the given current density.

Metal ion concentration: When fine deposits are required, a low metal ion concentration is desirable, so that no one crystal can grow rapidly. The metal ion concentration can be reduced by the following methods:

1. Use of dilute solutions: This is not much practical method as in the dilute solutions, on passing current, the concentration around the cathode increases, which causes rough deposits.
2. Use of complex salt; A complexing agent is added to the metal ion solution, so that a complex ion of the metal is formed. On electrolysis, the metal ion is formed from the complex ion as fast as they are removed by deposition.
3. Use of common ion: The metal ion concentration can be reduced by addition of a compound with common ion. eg. H_2SO_4 or Na_2SO_4 can be added to solution of CuSO_4 , so that the conductivity increases and produces desired effect on deposited metal.

Hydrogen ion concentration (pH): the position of the metal (to be deposited) in the emf series decides that the metal will plate out easily or with difficulty. The presence of H^+ ions in the desirable amount is needed for the clear deposition.

Eg. Cu and Zinc plates out easily in high concentration of H^+ ions i.e. at low pH.

Ni and Fe are plated out from nearly neutral solution.

Addition agents: Addition agents are substances added to an electrolyte solution in addition to those main constituents whose functions are known. Addition agents produce no marked effect on the conductance or on metal ion concentration. However, they certainly influence the nature of the deposits. Nearly all addition agents are colloids or reducing agents. Eg. Glue, glucose, quinine, peptone, oil of cloves etc. They reduce treeing (Depositing large crystals of metal) & cause fine deposits. The colloidal material is deposited with the metal which interferes the crystal growth.

Brighteners: Sometimes bright deposits are required for excellent reflecting power. Hence, some brighteners are added to the solution so that alternate parallel bands of the metal and the brighteners are deposited. Eg. Gelatin added to Cu soln. The brighteners can be anionic (Aromatic sulphonates, sulphonamides) OR cationic (Aldehydes, ketones, aromatic amines). But on combinations anionic and cationic brighteners together produce enhanced brightness.

Formulation of plating solns: Use of simple metal soln alone for electroplating produce dull, brittle & coarse deposits. Therefore, in modern plating, the bath is complex and had 6 to 8 constituents. Eg. Chlorides are added to promote anode dissolution. Boric acid and organic acid salts of alkali metals to act as a buffer (to maintain the pH) Some metals and organic brighteners to give luster & antipitting agents to prevent pin holing etc. Hence, the depositing solution must have following characteristics:

1. High metal content but low metal concentration.
2. Good conducting power.
3. Stability when in contact with the metals to be coated.
4. Effectivity in maintaining constant metal content of the solution.
5. Good throwing power.

Thickness of the deposit: The thickness of the deposit depends upon the current density, time & density of the deposited metal.

$$\text{Thickness in inches of deposit per hour} = \frac{C. D. \times \text{gm per amp hr}}{144 \times 16.4 \times \text{sp. Gravity}}$$

Electroplating Equipment:

Current generation: A low voltage D. C. current is generated near the plating plant. Mostly 6 volts will be sufficient. For chromium, 12 volts are needed.

Current distribution: The current is carried from the generator to the plating tank via copper bars.

Electrical measurement: Voltmeter or ammeter are used for regulating the current.

Tanks: Tanks are required for plating for rinsing / cleaning / electrocleaning and for actual plating purpose.

Wooden tanks are used for rinsing. Steel tanks are used for cleaning and electrocleaning. Steel tanks are used for alkaline baths. Lead lined steel tanks are used for acidic (H_2SO_4 and Chromic acid baths), Rubber lined tanks are used for neutral/acidic baths.

Agitation and motion plating: Agitation of the cathode is done mechanically or through automated machines or by using air.

Circulation and filtration: The anodes used in plating are not pure & therefore sludge will accumulate at the bottom of the tank or get suspended in tank which should be removed by filtration.

Preparation of articles for plating: The articles to be plated must be very clean. The foreign materials likely to be adhered to metallic surfaces are of 2 types: (1)organic substances like grease, oil& dirt. (2) oxides or related products of corrosion as scale, tarnish or rust.

a. Removal of greasy material: It is done by using organic solvents like gasoline, benzene & CCl_4 or by using alkaline solutions like NaOH , Na_2CO_3 , soap, Na_3PO_4 , Na_2SiO_3 , Borax etc. which emulsify the grease and wash away from metallic surfaces. The articles also can be electrocleaned using tank containing alkaline solution. The evolution of H_2 on the article (Which is made cathode) causes lifting up of the grease from articles.

b. Removal of scale & other oxides: Several methods are available for removal of scales and other oxides.

1. Pickling process: It is the process of cleaning the article in acid (HCl and H_2SO_4) Acid reacts with metal surface. There is liberation of H_2 gas. The bubbles of which lift the scales away.

2. Electrolytic removal of scale: The metal article is made cathode and dipped in acid bath of 30% H_2SO_4 and heated H_2 liberated washes away (Blasts off) the scales.
3. Sand blasting: Mechanical removal of scales by using sand is called sand blasting.
4. Wire brushes: Wire brushes with abrasives such as pumice, silicon carbide, emery are used in alkaline soln to remove scales.
5. Tumbling barrels: Small articles are cleaned in small tumbling barrels with sand, emery or suitable abrasive in wet or dry condition.
6. bright dipping: After cleaning the articles are further polished using acid baths by dipping method. H_2SO_4 and HNO_3 with some salt are used for bright dipping.
7. Electrolytic polishing: Electrolytic polishing involves the treatment of metallic surfaces in baths of sulphuric, chromic or phosphoric acid at high current density. The article is made anode so that spots are dissolved in the solution and the uniform level of surface is achieved.

Nickel plating:

Solution for nickel plating: Nickel ammonium sulphate 75 g/lit is universally used for nickel plating. Otherwise nickel chloride or carbonate also can be used. Zinc, copper and iron may be present in the nickel salts as impurities. The Cu & Zn are removed by neutralizing the nickel solution by NH_3 or NiCO_3 to $\text{pH} = 6.7$ & then filtering. Small quantity of iron (0.1%) is helpful to promote anode corrosion & prevent it from passivity.

$(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , Na_2SO_4 are added to increase the conductivity of the bath. Sulphates cause decrease in dissociation of NiSO_4 due to common ion effect.

Anode: Very pure Nickel anode is not generally used because it becomes passive in NiSO_4 soln. Hence some $(\text{NH}_4)_2\text{SO}_4$, NaCl , Fe and C are added to anode material to increase anode corrosion.

pH: Ni is above hydrogen in the emf series of elements. Hence it cannot be plated from strong acid solutions. PH less than 4 causes cracked deposits and higher than 6.5 causes dark curly deposits. Therefore, pH is maintained between 5-6 by adding buffer like boric acid.

Composition of the solution:

A. For general work: NiSO_4 (150 gm), boric acid (10 gm) NaCl (6 gm) water 1 lit.

B. Heavy solution for rapid deposition: NiSO_4 (300 gm), NiCl_2 (20gm), boric acid (12 gm), water 1 lit.

Temperature: For general work, cold or room temperature is usefull while, heavy deposition is done at 40°C .

Current density: For light soln: 6-8 amp per sq. feet. And 50-60 amps for heavy solns.

PH : 5-6 (5.2-5.8)

Mostly, the nickel plating is followed by chromium plating.

Bright Nickel plating: Articles must be rinsed and dried and polished 2, 3 times. Due to which 20% of the deposit is removed.

Addition agents: Na-formate, boric acid & other organic brighteners are used as additives.

Applications:

1. Nickel plating is one of the most important electroplating industries. It is used as a protective coat on steel, zinc and brass etc.
2. As a base for chromium plating.
3. To repair worn parts of engineering.
4. For electroforming printing plates, phonograph masters, sheet, tube & screen.

Chromium plating:

Chromium plating is done to provide brilliant untarnishable finish & to produce hard abrasion resistance to the surface.

Solution: Chromic acid, CrO_3 : 250 gm/lit., H_2SO_4 or sulphate: 25 gm/lit., water: 1 lit, **Temp:** 40-55°C. **Current density:** 90-235 amps/sq. ft.

The most important constituents of the bath are CrO_3 and SO_4^{2-} ions. The ions CrO_3 and SO_4^{2-} should be present in the bath in the ratio 100: 1 & for best throwing power it should be 200: 1 under ordinary conditions. The efficiency of plating is very low. Cathode efficiency is about 12.5%. So for proper electroplating of Cr, the correlation & control of soln composition, temperature, & current density are very important. As stated, when CrO_3 and SO_4^{2-} in the bath are in the proper proportion, satisfactory plating can be obtained when the temp is between 40-55 °C.

The current density must also be properly maintained for the temperature employed.

Chromium **anodes** are not used in the chromium plating. It is therefore more economical to supply chromium ions by introducing CrO_3 in the bath directly. The specific gravity of the soln is 1.18. Lead or steel anodes are used commercially. Lead anode is preferred, as it does not contaminate the bath. Anode area should be as large as possible.

During electroplating, H_2 is evolved at cathode and O_2 at anode. Hence, special ventilation is necessary. Periodical medical check up of the workers is also necessary.

Chromium plating is usually porous hence it is not the practice to deposit chromium directly on iron, steel, zinc or brass etc. Therefore it is plated over nickel plating.

Applications:

1. As a final finishing operation on many articles in general use.
2. Thin coating serves as a nontarnishing durable for decorative articles.
3. It gives brilliant bluish- white mirror like appearance.
4. Provides resistance to wear in printing plates, wrist pins, steering knuckles, dies etc.
5. For various engineering applications.